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Author: Eadaoin McCourt, Żaneta Wojnarowska, Johan Jacquemin, Peter Nockemann, Haresh G. Manyar, Łukasz Hawełek, Marian Paluch

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Temperature- and Pressure-Induced Structural Changes of Cobalt(II) in a Phosphonium-Based Ionic Liquid

Éadaoin McCourt,[†] Zaneta Wojnarowska,^{*,‡,§} Johan Jacquemin,[†] Peter Nockemann,[†] Haresh G. Manyar,[†] Lukasz Hawelek,^{||} and Marian Paluch^{‡,§}

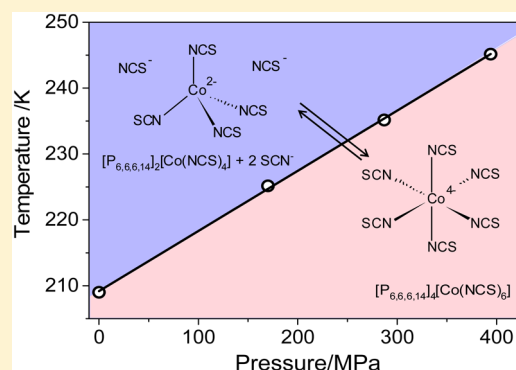
[†]The School of Chemistry and Chemical Engineering/QUILL Research Centre, Queen's University of Belfast, David Keir Building, Stranmillis Road, Belfast BT9 5AG, Northern Ireland, U.K.

[‡]Institute of Physics, University of Silesia, Uniwersytecka 4, 40-007 Katowice, Poland

[§]SMCEBI, 75 Pulku Piechoty 1A, 41-500 Chorzow, Poland

^{||}Institute of Non-Ferrous Metals, ul. Sowinskiego 5, 44-100 Gliwice, Poland

ABSTRACT: The temperature- and pressure-induced paramagnetic switching of cobalt(II) complex in a binary mixture of phosphonium-based ionic liquid $[P_{6,6,6,14}]SCN$ and $[Co(NCS)_2]$ is reported. This arises from a structural change in the coordination of the cobalt(II) center from tetrahedral $[Co(NCS)_4]^{2-}$ to octahedral $[Co(NCS)_6]^{4-}$ when mobile thiocyanate ions are added. These properties are reflected in the abrupt change of the conductivity behavior of the magnetic ionic liquid. Therefore, as demonstrated herein, the reversible switching in coordination of cobalt from tetrahedral to octahedral can be easily monitored at ambient as well as elevated pressure by tracking the dc-conductivity changes.



INTRODUCTION

Ionic liquids, classified as liquids composed solely of ions that have melting points below 100 °C, have been the subject of in-depth investigations in recent years.¹ This can be attributed to their unique physical properties which make them very attractive for many chemical and industrial applications. These include high conductivity, negligible vapor pressure, wide liquid range, and high thermal and physical stability.² An important subfield of ionic liquids is the field of magnetic ionic liquids (MILs). Besides the favorable properties of ionic liquids presented above, magnetic ionic liquids have, in addition, intrinsic magnetic properties due to the incorporation of transition metals into either the anion or cation structure. This incorporation has broadened the scope of these liquids especially in the field of materials chemistry.³ Adding transition metals opens the potential to control properties and impart additional functionalities. For example, because of the intrinsic magnetic properties of MILs, they have been considered as potential magnetorheological fluids, which are stimuli-responsive fluids that can, for example, change their viscosity by applying an external magnetic field.^{4,5}

Magnetic ionic liquids are a relatively new class of ionic liquids, first investigated by Yoshida et al.⁶ and Hayashi et al.,⁷ containing transition-metal-based anions, such as $[FeCl_4]^-$. Since their discovery, many other magnetic ionic liquid systems have been developed.^{8–11} In the majority of cases the anion has been composed of first row transition metals, Fe, Mn, Co and Ni, in monanionic halogenido complexes. Moving away from

halogen -containing ILs, known to have undesirable properties, those based on isothiocyanato-metalates have been developed by Peppel et al.¹⁰ and Del Sesto et al.¹² $[C_2mim]_2[Co(NCS)_4]$ and $[C_4mim]_2[Co(NCS)_4]$ were synthesized, and some initial analysis of their physical properties revealed low viscosities (145 cP at 25 °C) and good ionic conductivities (4.0×10^{-3} S cm^{-1} at 25 °C) despite the divalency of the anion.¹⁰

Investigations into the effect of external stimuli on the physical properties of MILs are relatively scarce. The intrinsic electrochromic behavior of ionic liquids based on ethylenediaminetetraacetic metal complex anions were investigated by Branco et al.;¹³ Funasako et al.¹⁴ investigated a series of metal chelate complex ionic liquids showing thermochromic changes in response to solvent vapors and gases; and Kohno et al.¹⁵ reported the thermoresponsive and selective water coordination of a cobalt(II) bis(salicylate)-based ionic liquid. Recently, the potential to manipulate the physical properties of MILs using temperature as a stimulant was investigated by Osborne et al.¹⁶ Ultraviolet–visible spectroscopy and superconducting quantum interference device measurements were used to report the reversible switching of cobalt coordination from tetrahedral $[Co(NCS)_4]^{2-}$ to octahedral $[Co(NCS)_6]^{4-}$ with neat imidazolium-based cation, resulting in a change in the magnetic susceptibility and color from blue to pink upon cooling. The

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structural characterization of the octahedral complex $[\text{Co}(\text{NCS})_6]^{4-}$ has been previously reported by Mali et al., and it was seen to be bright red in color.¹⁷ Switchable properties such as those discussed above are important in various applications. In particular, switchable magnetic properties are recognized as key components for the next generation of data storage and processing devices.¹⁸

In this work, we investigate the physicochemical properties of cobalt thiocyanate salt, $\text{Co}(\text{NCS})_2$, in different mole ratios of $[\text{P}_{6,6,6,14}][\text{SCN}]$ ionic liquid and various T – P conditions. The studies of conductivity behavior of $[\text{P}_{6,6,6,14}][\text{SCN}]/[\text{Co}(\text{NCS})_2]$ mixture over a wide temperature (193–403 K) and pressure ranges (0.1–600 MPa) combined with calorimetric [differential scanning calorimetry (DSC)] and structural [X-ray diffraction (XRD)] investigations enable us to provide new insight into the field of magnetic ionic liquids. In this case, we explore the effects of pressure as a stimulant in inducing changes in the structure of the magnetic ionic liquid described above. The results presented herein go a long way in delivering the answers to two important questions, namely, (i) *Is it possible to recognize changes in the structural properties of $[\text{P}_{6,6,6,14}][\text{SCN}]/\text{Co}(\text{NCS})_2$ from its conductivity behavior?* (ii) *Is it possible to induce changes in the coordination geometry of a cobalt complex through the use of high pressure?*

■ EXPERIMENTAL SECTION

Potassium thiocyanate, KSCN; cobalt thiocyanate, $\text{Co}(\text{NCS})_2$; absolute ethanol with purity >99.5%; and acetone purists >99% were purchased from Sigma-Aldrich and used without further purification. Trihexyltetradecylphosphonium chloride was synthesized in QUILL, Queens University Belfast.

Synthesis and Purification of $[\text{P}_{6,6,6,14}][\text{SCN}]$. Trihexyltetra(decyl)phosphonium thiocyanate was prepared by reaction of equimolar amounts of trihexyltetra(decyl)phosphonium chloride, $[\text{P}_{6,6,6,14}]\text{Cl}$, and potassium thiocyanate, KSCN. In separate round-bottom flasks, $[\text{P}_{6,6,6,14}]\text{Cl}$ (6 g, 0.012 mol) was added to 10 mL of acetone and KSCN (1.123 g, 0.012 mol) in 10 mL of acetone. When fully dissolved, the reagents were added together, forming a milky white solution, and the solution was left to stir at room temperature overnight. KCl was filtered off, and acetone was removed by rotary evaporator. The resulting ionic liquid was washed twice with deionized water and dried under vacuum for 24 h at 70 °C.

Elemental analysis: $[\text{P}_{6,6,6,14}][\text{SCN}]$. Theoretical %: C, 73.14; H, 12.65; N, 2.58; S, 5.92. Actual %: C, 72.90; H, 12.77; N, 2.53; S, 5.98.

Karl Fischer was used to analyze the water content in the prepared ionic liquid. The sample contained 660 ppm water.

Synthesis of $[\text{P}_{6,6,6,14}][\text{Co}(\text{NCS})_4]$ with Excess Ionic Liquid. Different mole ratios of ionic liquid, $[\text{P}_{6,6,6,14}][\text{SCN}]$ to salt, $\text{Co}(\text{NCS})_2$, were reacted together in a 50 cm³ round-bottom flask with magnetic stirrer. Absolute ethanol was used as cosolvent. When the reaction was homogeneous, the ionic liquid was freed of solvent and dried under vacuum overnight at 85 °C.

Elemental analysis: $[\text{P}_{6,6,6,14}][\text{SCN}] + \text{Co}(\text{NCS})_2$ (10:1). Theoretical %: C, 71.28; H, 12.25; N, 3; S, 6.88. Actual %: C, 71.00; H, 12.59; N, 2.95; S, 6.51.

Karl Fischer analysis determined a water content of 710 ppm.

Dielectric Measurements. Broadband dielectric spectroscopic ambient pressure measurements were carried out on a Novo-Control GMBH alpha analyzer in the frequency range of 10^{-1} – 10^6 Hz. The sample was placed between two stainless

steel electrodes, and the temperature was measured from 193 to 403 K in different heating steps controlled using a Novo-Control Quattro system with a liquid nitrogen cryostat. Temperature stability was greater than 0.1 K. High-pressure dielectric measurements were performed by placing the capacitor, containing the sample of interest, in a high-pressure chamber and compressing it using silicone oil. Low-temperature measurements were enabled using a Weiss fridge. During the high-pressure measurements, the sample was in contact only with stainless steel and Teflon. The sample was heated to 423 K prior to measurements to remove traces of water from the sample.

The protocol of ambient and high-pressure measurements had two steps. First, the dielectric response of the sample was recorded during isobaric cooling [or isothermal compression in the case of high-pressure broadband dielectric spectroscopy (BDS) measurements]. After that, the dielectric spectra of the studied IL were collected during heating (decompression) starting with low temperature and high pressure, respectively.

Calorimetric Measurements. The calorimetric measurements were carried out using a Mettler-Toledo DSC apparatus equipped with a liquid nitrogen cooling accessory and an HSS8 ceramic sensor (heat flux sensor with 120 thermocouples). The cooling system enabled the heat flow to be measured at temperatures as low as 133 K.

X-ray Diffraction. Temperature-dependent XRD experiments were performed on a Rigaku-Denki D/MAX RAPID II-R diffractometer (Rigaku Corporation, Tokyo, Japan) equipped with a rotating anode Ag $K\alpha$ tube ($\lambda = 0.5608$ Å), an incident beam (002) graphite monochromator, and an image plate in the Debye–Scherrer geometry. The pixel size was $100 \mu\text{m} \times 100 \mu\text{m}$. Studied samples were placed inside glass capillaries (1.5 mm in diameter). The temperature was controlled using the Oxford 700 Series Cryostream Cooler with the proven temperature stability of 0.1 K. The measurements were performed on sample-filled and empty capillaries, and the background intensity of the empty capillary was subtracted from the sample signal. The beam width at the sample was 0.3 mm. The two-dimensional diffraction patterns were converted into one-dimensional intensity data using suitable software.

■ RESULTS AND DISCUSSION

To investigate the conductivity behavior of the examined magnetic ionic liquid, we took advantage of broadband dielectric spectroscopy, a technique traditionally employed for studying the molecular dynamics of glass-forming systems. According to standard practice, the dielectric response of the studied IL is analyzed in electric conductivity formalism $\sigma^*(f) = \epsilon_0/Z^*(f)C_0$, with the frequency f covering the range from 10^{-1} to 10^6 Hz and C_0 being the capacity of the empty capacitor.

The frequency-dependent conductivity plot of $[\text{P}_{6,6,6,14}][\text{SCN}] + \text{Co}(\text{NCS})_2$ (mole ratio 10:1) is presented in Figure 1. As can be easily seen, the real part of the complex conductivity function (σ') is characterized by a frequency-independent part which gives directly the dc-conductivity value of the studied system.

From this graph, it is apparent that as the ionic liquid system is cooled, a shift in the dc-conductivity to lower values is observed. This gradual change is in keeping with the effects of cooling seen in other ionic liquid systems, and it is connected with suppressed mobility of ions. However, in contrast to other ionic conductors at 209 K, a sudden drop in dc-conductivity is

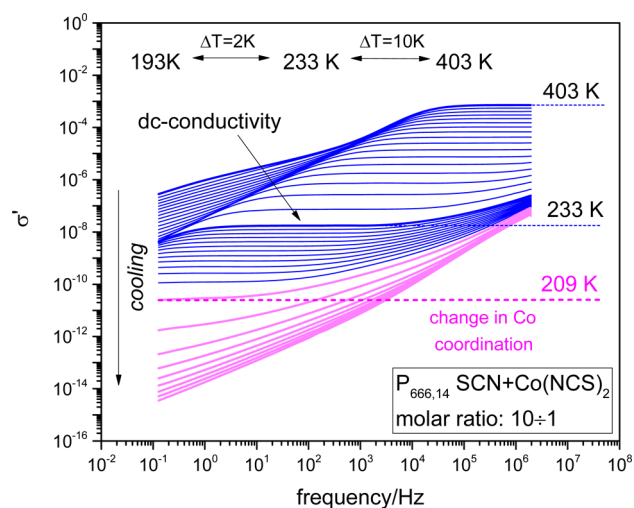


Figure 1. Conductivity behavior of $\text{Co}(\text{NCS})_2$ in excess ionic liquid $[\text{P}_{6,6,6,14}]\text{SCN}$ (1:10) presented over a frequency range from 10^{-1} to 10^6 Hz.

observed. Importantly, the shape of $\sigma'(f)$ spectra as well as the value of dc-conductivity recorded during the subsequent heating from 193 K are exactly the same as that obtained during the first (cooling) step. Therefore, one can certainly say that the observed effect is reversible. To characterize this phenomenon in more detail, the values of σ_{dc} are plotted as a function of inverse temperature in Figure 2.

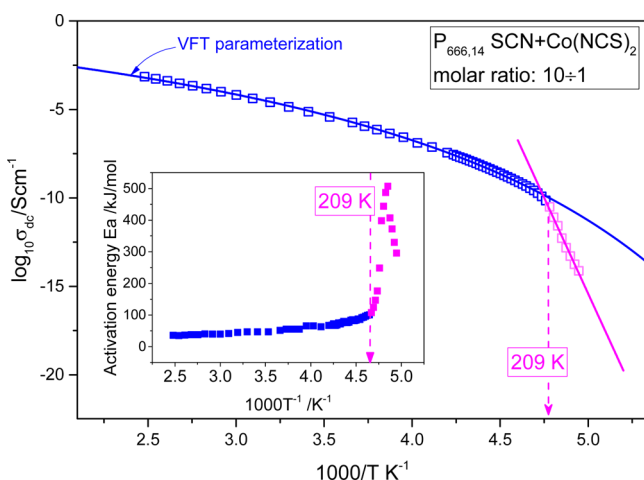


Figure 2. Temperature dependence of dc-conductivity presented in the temperature range 403–202 K. Solid line is the VFT with the following parameters: $\log \sigma_{\infty} = -0.44$, $D = 13.32$, and $T_0 = 130$. Inset panel presents the activation energy as a function of inverse of temperature.

A number of points can be taken from this graph. The first is that upon cooling the conductivity data reveals non-Arrhenius behavior that can be well-parametrized by means of the Vogel–Fulcher–Tammann (VFT) equation:^{19–21}

$$\log \sigma_{\text{dc}} = \log \sigma_{\infty} + \frac{DT_0}{T - T_0} \log e \quad (1)$$

where σ_{dc} is the dc-conductivity, D the material constant, and T_0 the temperature usually regarded as the “ideal” glass temperature.

The second, conditions where the $\sigma'(f)$ spectra become much more sensitive on cooling, an evident deviation of $\sigma_{\text{dc}}(T)$ points from the VFT law is observed. For the first sight, such behavior could be related to liquid–glass transition. However, according to the literature, generally T_g of ionic glass-formers is manifested by the characteristic crossover of temperature dependences of σ_{dc} from VFT-like to Arrhenius behavior around 10^{-15} S/cm (σ_{dc} at T_g can be higher in the case of protic ionic liquids and solids^{22,23}). Additionally, the activation energy (as well as entropy) of ion dynamics in the glassy region is always much lower than E_a typical for the supercooled liquid state.²⁴ As can be seen in the inset in Figure 2, the activation energy parameter of $[\text{P}_{6,6,6,14}][\text{SCN}] + \text{Co}(\text{NCS})_2$ calculated from the equation

$$E_a = -2.303R \left. \frac{\partial \log \sigma_{\text{dc}}}{\partial (T^{-1})} \right|_{P=0.1 \text{ MPa}} \quad (2)$$

drastically increases above 209 K, and it reaches values even 5-times higher than those determined in the supercooled region. Therefore, one can surely say that the observed change in σ_{dc} behavior is not a manifestation of the liquid–glass transition. This is additionally confirmed by results obtained from differential scanning calorimetry studies. The DSC thermogram recorded during cooling of examined IL, from 375 K down to 133 K with a rate of 10 K/min, reveals a small exothermic peak around 210 K. Note that at the same temperature the dramatic drop of σ_{dc} occurs. The closer inspection of DSC data also exhibits the existence of a steplike change in the heat flow curve at 155 K. This effect can be associated with the liquid–glass transition of studied IL (see upper panel of Figure 3). On the

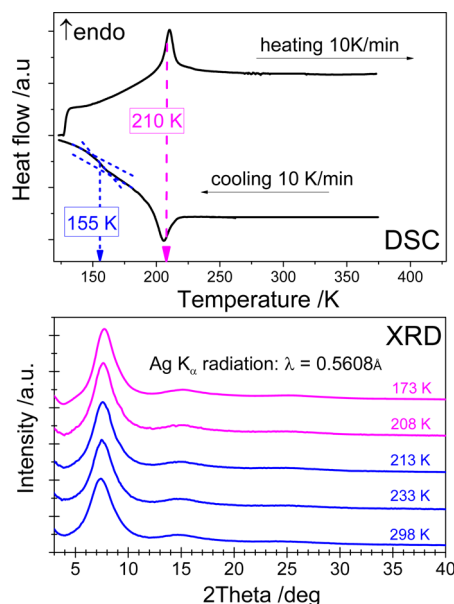


Figure 3. Results of DSC measurements (upper panel) and XRD measurements (lower panel).

other hand, during the subsequent heating of the studied IL, a small endothermic peak appears. Interestingly, a similar result has been reported for an iron(II) system undergoing a spin transition.¹⁶ Because both cooling and heating scans of $[\text{P}_{6,6,6,14}][\text{SCN}] + \text{Co}(\text{NCS})_2$ (mole ratio 10:1) did not reveal any signs of cold crystallization, one can state that it remains disordered throughout the entire examined temperature range.

This has been also confirmed by the results of the XRD method. As presented in the lower panel of Figure 3, the XRD data collected over a wide temperature range take the form of broad halo without any Bragg peaks that are characteristic for the crystalline state. Taking these facts together, one can state that the sharp change in conductivity of the $[P_{6,6,6,14}][SCN] + Co(NCS)_2$ (mole ratio 10:1) sample observed at 209 K is a result of a reversible change in the coordination of the cobalt center.

As previously reported for other magnetic ionic systems, at room temperature the cobalt(II) center preferably forms a tetrahedral complex.¹⁶ However, if an excess of ionic liquid is added and the temperature is decreased, there is the possibility for the cobalt center to change its equilibrium position and rearrange to form an octahedral complex. Because the size of the octahedral complex is increased and its charge changes from -2 (tetrahedral) to -4 (octahedral), its lower mobility compared with the tetrahedral form may be expected. Therefore, cobalt changing from tetrahedral to octahedral could result in a lowering of conductivity, as suggested by Figure 2.

Although rapid cooling is probably the simplest method for inducing changes in the magnetic properties of the ionic liquid, it does not mean that this is the only route. García-Saiz et al.²⁵ previously explored the properties of $Emim[FeCl_4]$ showing a transition from antiferromagnetic to ferromagnetic three-dimensional ordering under hydrostatic pressure. In this context, one may question the possibility of manipulating the cobalt coordination by means of isothermal compression.

To shed more light on this issue, high-pressure BDS experiments of $[P_{6,6,6,14}][SCN]/Co(NCS)_2$ mixture were performed isothermally at 225, 235, and 245 K. Representative results are presented in Figure 4.

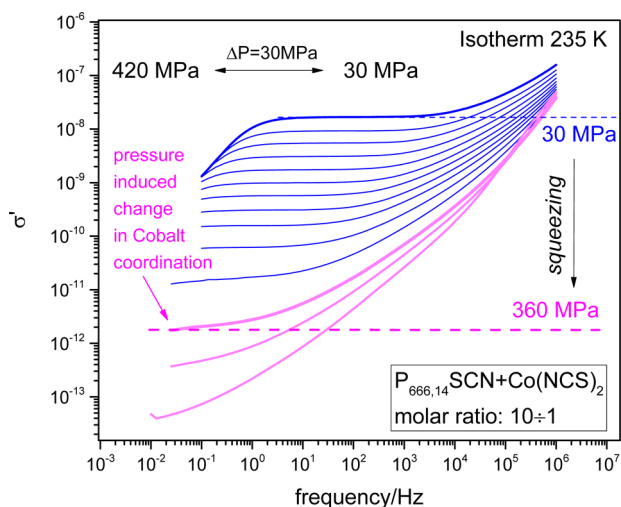


Figure 4. Dielectric spectrum presented in conductivity representation in the form of frequency-dependent data under pressure.

Interestingly, when $[P_{6,6,6,14}][SCN] + Co(NCS)_2$ (mole ratio 10:1) is compressed, the same pattern of $\sigma'(f)$ behavior as during isobaric cooling is observed, i.e., despite the same pressure step, suddenly the σ_{dc} value gets markedly lower. This is clearly visible in Figure 5 as a characteristic crossover of $\sigma_{dc}(P)$ experimental points from one linear behavior to another. Because in both these regions the dc-conductivity varies with

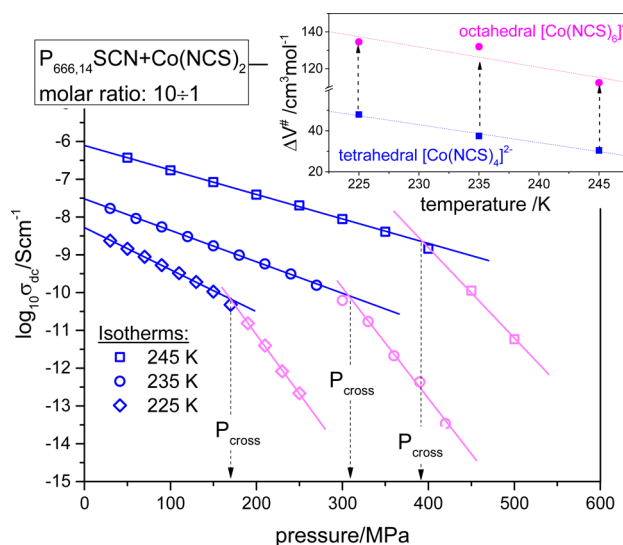


Figure 5. Effects of pressure on dc-conductivity behavior of $[P_{6,6,6,14}][SCN] + Co(NCS)_2$ (10:1). The inset presents the temperature dependence of activation volume parameter.

pressure in a linear fashion, it can be well-parametrized by means of a volume-activated law:

$$\log \sigma_{dc}(P) = \log \sigma_0 + \frac{P\Delta V^\#}{RT} \quad (3)$$

with $\log \sigma_0$ being the value of dc-conductivity at atmospheric pressure, R the universal gas constant, and $\Delta V^\#$ an apparent activation volume commonly related to the local volume expansion required for ionic transport.^{26,27} As one can see in the inset to Figure 5, the activation volume coefficients determined for $[P_{6,6,6,14}][SCN] + Co(NCS)_2$ (mole ratio 10:1) system in the $P < P_{cross}$ range is relatively low, thereby reflecting the weak change in dc-conductivity of the studied IL with squeezing. Moreover, it was found to decrease with increasing temperature (from 48 cm³/mol at 225 K to 30 cm³/mol at 245 K), which is typical for many other ionic and nonionized materials and is considered as a specific feature of the dynamics of supercooled liquids and amorphous polymers. However, much more important information coming from the inset to Figure 5 is the markedly higher value of the apparent activation volume determined above the P_{cross} .

Because $\Delta V^\#$ is defined as the local volume required for ionic transport, one can expect that the molecular dimension of conducting species in the region above P_{cross} should be larger than that below P_{cross} . Such a scenario comes true only if the switching of cobalt coordination from tetrahedral $[Co(NCS)_4]^{2-}$ to octahedral $[Co(NCS)_6]^{4-}$ occurs. This is a clear proof that the kink of the $\sigma_{dc}-P$ as well as $\sigma_{dc}-T$ curves can be treated as a manifestation of changes in the coordination of a cobalt isothiocyanate complex.

To determine the phase transition line between the tetrahedral and octahedral cobalt complex in the next step, the crossover temperature, T_{cross} , is plotted as a function of pressure. As depicted in Figure 6, the T_{cross} rapidly increases with squeezing in linear fashion. Thus, the slope of $T_{cross}(P)$ curve, equal to 0.09 K/MPa, reflects the pressure sensitivity of Co coordination changes. It means that an increase of pressure in the order of 100 MPa raises T_{cross} by 9 K. Consequently, to realize the coordination change of cobalt in the examined MIL

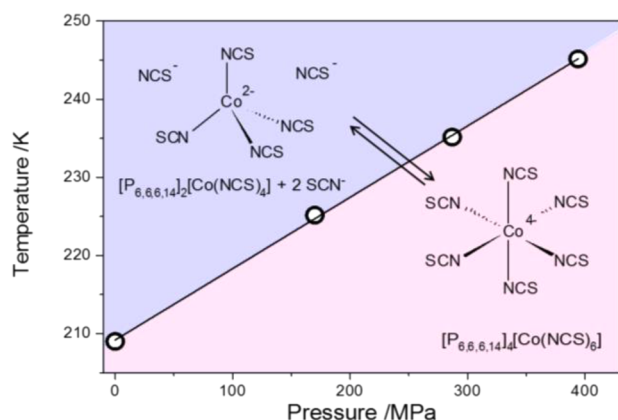


Figure 6. Phase diagram of $[P_{6,6,6,14}][SCN] + Co(NCS)_2$ (10:1).

under high-pressure conditions, temperatures as low as 209 K are no longer required.

CONCLUSIONS

The results of this work show how the properties of magnetic ionic liquids can be tailored using external stimuli. In this case, the effects of temperature and for the first time pressure on inducing changes in the coordination of a cobalt isothiocyanate complex in a neat ionic liquid system are reported. Most importantly, the effects of hydrostatic pressure in the range of 0.1–600 MPa in inducing this change in coordination ability of Co(II) has been proven. BDS spectroscopy is a powerful and versatile tool to reveal stimuli responsive structural changes through conductivity behavior. The mobility of ions in ionic liquid media in a large temperature and pressure window provides a unique environment to study stimuli-induced coordination changes. The results of this work provide an exciting introduction to the potential switchable properties of transition-metal-based ionic liquids and opens this field for further investigations.

AUTHOR INFORMATION

Corresponding Author

*E-mail: zwojnaro@us.edu.pl. Phone: +48 323497629.

Notes

The authors declare no competing financial interest.

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